

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/GB05/000373

International filing date: 03 February 2005 (03.02.2005)

Document type: Certified copy of priority document

Document details: Country/Office: GB
Number: 0402395.8
Filing date: 03 February 2004 (03.02.2004)

Date of receipt at the International Bureau: 04 April 2005 (04.04.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse



PCT/GB 2005 / 0 0 0 3 7 3



INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

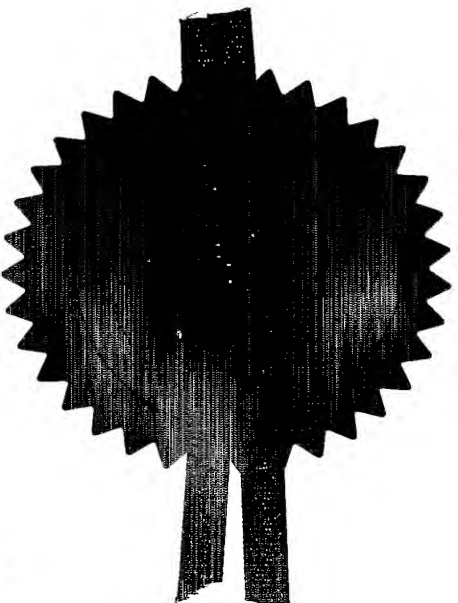
In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed *William Morell*

Dated 15 March 2005



Patents Form 1/77

Patents Act 1977
(Rule 16)

The Patent Office

THE PATENT OFFICE
K

- 3 FEB 2004

RULE 97
NEWPORT

1/77

The Patent Office

Cardiff Road
Newport
South Wales NP10 8QQ

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet, from the Patent Office to help you fill in this form)

1.	Your reference	CDK2158	04FEB04 E870529-1 D02806
2.	Patent application number (The Patent Office will fill in this part)	0402395.8	P01/7700 0.00-0402395.8 NONE
3.	Full name, address and postcode of the or of each applicant (underline all surnames)	RHODIA CONSUMER SPECIALTIES LIMITED Oak House Reeds Crescent Watford Hertfordshire, WD24 4QP	
	Patents ADP number (if you know it)	7870322006	
	If the applicant is a corporate body, give the country/state of its incorporation	England	
4.	Title of the invention	SYNERGISTIC BIOCIDAL COMPOSITIONS	
5.	Name of your agent (if you have one)	Barker Brettell	
	"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	138 Hagley Road Edgbaston Birmingham B16 9PW	
	Patents ADP number (if you know it)	7442494002	
6.	Priority: Complete this section if you are declaring priority from one or more earlier patent applications, filed in the last 12 months.	Country	Priority application number (if you know it)
			Date of Filing (day/month/year)
7.	Divisionals, etc: Complete this section only if this application is a divisional application or resulted from an entitlement dispute (see note f)	Number of earlier application	Date of filing (day/month/year)
8.	Is a Patents Form 7/77 (Statement of inventorship and of right to grant of a patent) required in support of this request? Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. Otherwise answer NO (See note(d))	YES	

Patents Form 1/77

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.
Do not count copies of the same document
- Continuation sheets of this form

Description 6 + 6

Claim(s)

Abstract

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination
(*Patents Form 9/77*)

Request for substantive examination
(*Patents Form 10/77*)

Any other documents
(*please specify*)

11. I/We request the grant of a patent on the basis of this application.

Signature

Barker Brettell
Barker Brettell

Date

02 February 2004

12. Name and daytime telephone number of person to contact in the United Kingdom

Lucy P. Trueman

Tel: 0121 456 1364

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 01645 500505
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

Patents Form 1/77

SYNERGISTIC BIOCIDAL COMPOSITIONS

This invention relates to synergistic biocidal compositions.

- 5 The present invention is a selection invention relative to our published P.C.T. application WO 99/33345.

The said WO 99/33345 discloses synergistic biocidal compositions comprising "THP", a non-surfactant biopenetrant compatible with "THP"
10 and optionally a surfactant.

The term "THP" is defined in WO 99/33345 as meaning either a tetrakis(hydroxyalkyl)phosphonium salt or a tris(hydroxyalkyl)phosphine. To avoid confusion we shall hereinafter refer to "THP salts" or "THP"
15 respectively.

Examples of non-surfactant biopenetrants disclosed in the said WO 99/33345 include phosphonated derivatives of carboxylic acids, for example the phosphonated telomers disclosed in our published
20 European applications EP-A-0 491 391 and EP-A-0 861 846.

Other non-surfactant biopenetrants disclosed in the said WO 99/33345 include a copolymer of N, N, N', N'-tetramethyl-1,2-diaminoethane with bis(2-chloroethyl)ether. This is commercially available under the trade
25 name WSCP and will hereinafter be so referred to.

Where surfactants are used, examples disclosed in the said WO 99/33345 include sulphonated (anionic) surfactants and cationic surfactants such as those based on quaternary ammonium compounds, as well as non-ionic,
30 amphoteric and semi-polar surfactants.

We have now unexpectedly found that where the biopenetrant is a phosphonic acid-tipped polymer or copolymer, it acts synergistically with a THP salt to considerably enhance the biocidal efficacy of the THP salt against both planktonic (free-swimming) and sessile (attached) bacteria.

5

Accordingly, the present invention provides a synergistic biocidal composition comprising

- (i) a THP salt (as hereinbefore defined) and
- 10 (ii) a biopenetrant,

in which the biopenetrant comprises a polymer of an unsaturated carboxylic acid or a copolymer of an unsaturated carboxylic acid with a sulphonic acid, said polymer or copolymer being terminated by a mono-or
15 di-phosphonated unsaturated carboxylic acid.

Preferably, the THP salt is tetrakis(hydroxymethyl)phosphonium sulphate (THPS). Other THP salts include the phosphite, bromide, fluoride, chloride, phosphate, carbonate, acetate, formate, citrate, borate, or
20 silicate.

In accordance with preferred embodiments of the present invention, the biopenetrant may be a polyacrylate terminated with vinylphosphonic acid, (hereinafter "VPA end-capped polymer") or with vinylidene-1, 1-diphosphonic acid (hereinafter "VDPA end-capped polymer").
25

Alternatively, the biopenetrant may be an acrylate/sulphonate copolymer terminated with vinylidene-1, 1-diphosphonic acid (hereinafter "VDPA end-capped copolymer") or with vinylphosphonic acid (hereinafter "VPA
30 end-capped co-polymer").

The preferred ratio of VPA polymer or VDPA copolymer to THP salt, in accordance with the present invention, is in the range 1 to 10%, preferably 2 to 8%, most preferably 3 to 5%, (based upon a 50% THP salt formulation).

5

We have found that the compositions according to the present invention are equally effective in reducing the level of general heterotrophic bacteria and of sulphate reducing bacteria in waters.

10 The present invention will be illustrated by way of the following examples.

In the examples, the various abbreviations have the following meaning:

15 VPA polymer: a vinylphosphonic acid-terminated polyacrylate of molecular weight about 4000

VDPA copolymer: a vinylidene-diphosphonic acid-terminated
acrylate/sulphonate copolymer of molecular weight
20 6000-8000, typically about 7200.

GHB: general heterotrophic bacteria

SRB: sulphate reducing bacteria

25

WHO water: World Health Organisation Standard Hardness Water
(see TABLE I below)

SMOW water: Standard Mean Ocean Water (see TABLE II below)

30

THPS: a 50% aqueous solution of
tetrakis(hydroxymethyl)phosphonium sulphate

5

WSCP: copolymer of N, N, N', N'-tetramethyl-1,2-diamino
ethane and bis(2-chloroethyl)ether.

TABLE I WHO Standard Hardness Water	
1 litre contains:	
CaCl ₂ (anhydrous)	0.305 g
MgCl ₂ .6H ₂ O	0.139 g

10

TABLE II Standard Mean Ocean Water	
5 litres contain:	
NaCl	122.65 g
MgCl ₂ .6H ₂ O	55.52 g
Na ₂ SO ₄	20.45 g
CaCl ₂ .2H ₂ O	7.69 g
KCl	3.48 g
NaHCO ₃	1.00 g
KBr	0.50g
pH adjusted to 8.2 by means of 0.1N NaOH	

Example 1**Quantitative Suspension Test (Planktonic Bacteria) in WHO water**

5	Test Product	Log Reduction of General Heterotrophic Bacteria (based upon 50ppm ai THPS)	
		1 hour contact period	3 hour contact
10	Control	0	0
	Unformulated THPS	1	5.8
	THPS/VPA polymer*	7.4	Total kill
	THPS/VDPA polymer*	7.4	Total kill
	THPS/0.7% WSCP	3.7	7.4

15

Example 2**Quantitative Suspension Test in Deinking water**

20	Test Product	Log reduction values for 75ppm ai THPS/3 hour contact	
		GHB	SRB
	Control	0	0
25	Unformulated THPS	3.8	3
	THPS/VPA polymer*	5.1	3

Example 3**Biofilm (sessile) tests: freshwater (WHO)**

30

Test Product

Viable bacteria (GHB) after 75ppm ai THPS dosed for 3 hours

	Control	1×10^5
5	Unformulated THPS	1×10^5
	THPS/VPA polymer*-----	1×10^2
	THPS/VDPA polymer*	< 10
	THPS/2% sulphonated surfactant (a)	1×10^3

10 **Example 4**

Biofilm tests: seawater (SMOW)

Test Product

Viable bacteria after 75ppm ai THPS dosed for 3 hours

15

		GHB	SRB
	Control	1×10^4	1×10^6
	Unformulated THPS	1×10^2	1×10^4
20	THPS/VPA polymer*	< 10	< 10
	THPS/VDPA polymer*	1×10^2	1×10^2
	THPS/5% quaternary ammonium compound(b)	1×10^2	1×10^3

*In each case, the ratio of THPS to "polymer" was 50% a.i. THPS to 5% "polymer", the "polymer" comprising 25% solids as the sodium salt.

(a) A di-sodium salt of a mixed mono- and di-alkyl disulphonated diphenyl oxide, available as DOWFAX® 2A1.

30 (b) An alkyl dimethyl benzyl ammonium chloride, available as EMPIGEN®BAC 50.

